ULTRASONIC ABSORPTION IN CRYSTALLINE CYCLOHEXANE

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Submitted in partial fulfillment of
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IN
PHYSICS

United States Naval Postgraduate School
Monterey, California

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ABSTRACT

An investigation of the ultrasonic absorption properties of crystalline cyclohexane was conducted using an ultrasonic pulse technique. In addition, measurements of the velocity of acoustic waves were made in the specimens tested. Absorption and velocity measurements made on lucite and polystyrene are found to be in good agreement with published values. Graphical analysis of absorption measurements for cyclohexane at frequencies of 2.3, 3.85 and 9.3 megacycles per second shows that the attenuation constant varies as the two-thirds power of the applied frequency. The mechanism causing this absorption in cyclohexane is unknown. Pulse time delay measurements give a constant velocity for ultrasonic waves in cyclohexane of 1520 meters per second.

The writers wish to express their appreciation for the guidance and assistance given them by Professor O. B. Wilson of the U. S. Naval Postgraduate School during this investigation.

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1. Introduction.

The loss of acoustic energy during the propagation of acoustic waves through a solid medium may be divided into two classes; losses due to boundary conditions, and losses due to the dissipation of energy within the medium itself. During the course of this investigation, samples were selected to minimize boundary conditions, so as to permit measurements of absorptive processes taking place within the medium. Losses within the medium may be caused by several mechanisms. Among them are viscous processes, heat conduction, scattering reflections and relaxation processes involving molecular exchanges of energy. The viscous losses result from relative motion occurring between various portions of the medium during the compressions and expansions that accompany the transmission of a sound wave. Heat conduction losses arise from heat flowing from a hotter part of the medium to a cooler part. Viscous process losses as well as heat conduction losses are usually of a minor consequence for a rigid medium possessing high attenuation. Another acoustic effect is the loss to the scattering of sound when the sound wave length is of the same order of magnitude as the grain size in a polycrystalline material. This loss mechanism is an important one at high frequencies and has been shown to be proportional to the fourth power of the applied frequency when the wave length is three times or more the grain size. If, however, the wave length becomes comparable to the grain size, the fourth power law no longer holds, and when the grain size gets large compared to the wave length, the sound transmission becomes similar to a diffusion process and the losses should be proportional to the mean free path.

The dissipation of acoustic energy that is associated with the molecular structure of the medium results from the conversion of a portion of

the compressional energy of the medium to internal energy of molecular vibration. If the period of the acoustic cycle is comparable with the time required to establish equilibrium between lattice energy states and the internal states of the molecule, a fraction of the internal energy is retained by the molecules and is lost from the acoustic wave. This type of dissipation is only significant over particular frequency ranges, and has been offered as an explanation of several abnormally high values of absorption. Liebermann (3) has shown this type of resonance absorption phenomenon occurs in crystalline benzene. In general, the resonance absorption is proportional to the square of the applied frequency at frequencies below the relaxation frequency.

The investigation of the attenuation in solid cyclohexane was suggested by Liebermann (4) to determine whether this material, similar to benzene in many of its properties, would exhibit the molecular resonance absorption observed in benzene. Liebermann's theory of this process indicates that the absorption coefficient α, as defined by $I_x = e^{-2\alpha x}$, should be directly proportional to the square of the frequency, where I is the intensity of a plane compressional traveling acoustic wave.

2. Experimental Methods.

To investigate relaxations in solids, three basic methods are applicable (2). At lower frequencies (1 to 700 kilocycles) the method involves generating guided waves in a rod or bar by means of transducers, and observing the resonant frequency and the damping factor of the vibrations of the bar. A second method utilizes the measurement of transducer electrical input impedance changes produced by the mechanical loading. Impedance techniques are largely restricted to measurement of highly attenuating materials such as rubber-like polymers. A third type of measurement employed is the transmission and reflection of waves in an effectively infinite medium; it is often referred to as the ultrasonic pulsing method. By observing the rate of attenuation of reflections, the internal absorption of the material can be measured. The use of different sample lengths is required for materials of greater acoustical absorption.

The method used in this investigation is a variation of this last mentioned technique and involves detection of the direct pulse of sound waves by a second transducer that is matched with the driving transducer. It is assumed that the acoustic stress generated in the medium is proportional to the applied voltage at the driving transducer and that the transmitted acoustic stress is proportional to the output voltage of the receiving transducer. This assumption requires a good mechanical joint between transducer and sample as well as a pulse that is short enough so that the boundaries are effectively farther than one pulse length away. The mechanical joint between the specimen and transducer is made with a thin seal of silicone grease (Dow Corning High Vacuum Grease). The reproducibility of the results indicates that a good mechanical joint is not difficult to obtain. A pulse length of 4-5 microseconds is ordinarily employed.

The use of different sample lengths for attenuation measurements minimizes many of the unknown quantities of measurements utilizing a single sample; especially significant again would be the coupling of the mechanical joint between transducer and sample. By varying sample length, while using the same driving voltage, α can be computed from the measured change in the received voltage and change in length of the propagation path according to the formula, $\alpha = \frac{\ln V_1/V_2}{\Delta x}$ $cm.^{-1}$, where V is the receiver output voltage for a sample length of x centimeters. The velocity determinations are calculated from the measured sample length and the time delay between the leading edge of the transmitted and received pulses.

The block diagram of the pulse system used for measuring ultrasonic attenuations in solid material is shown in Figure 1. A variable frequency oscillator is the source of the carrier frequency. This is sent through a variable tuned pulsed RF amplifier that supplies about 15 volts at 100 ohms across the transducer. The amplifier is normally cut off by a negative bias applied to the first grid of the output tube. The pulses applied to the grid remove the bias and allow an alternating current pulse for a controllable number of cycles to be applied to the driving transducer. The pulse generator also emits a synchronizing trigger pulse to the oscilloscope sweep. The oscilloscope is used to present both the driving signals and the output signals. A camera is used to record the presentation.

The transducers employed are barium titanate ferroelectric ceramics which, when polarized, are capable of converting electrical energy into mechanical energy and vice versa. Fundamental frequencies above one megacycle are usually generated by thickness vibrations according to the relation $t = \lambda/2 = c/2f$, where λ is the acoustic wave length and c is

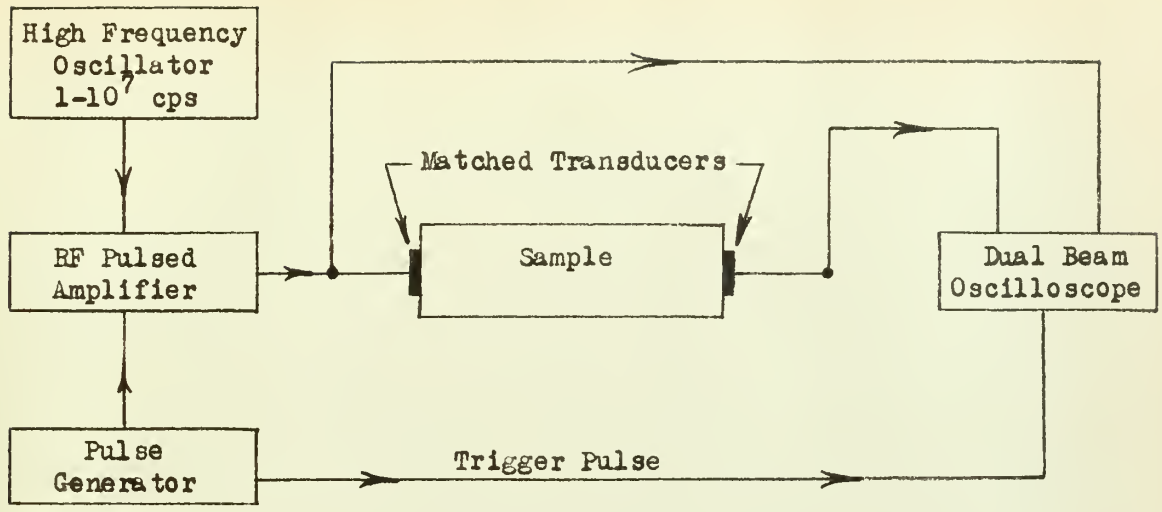

Figure 1. A pulse system for measuring attenuation in a solid material.

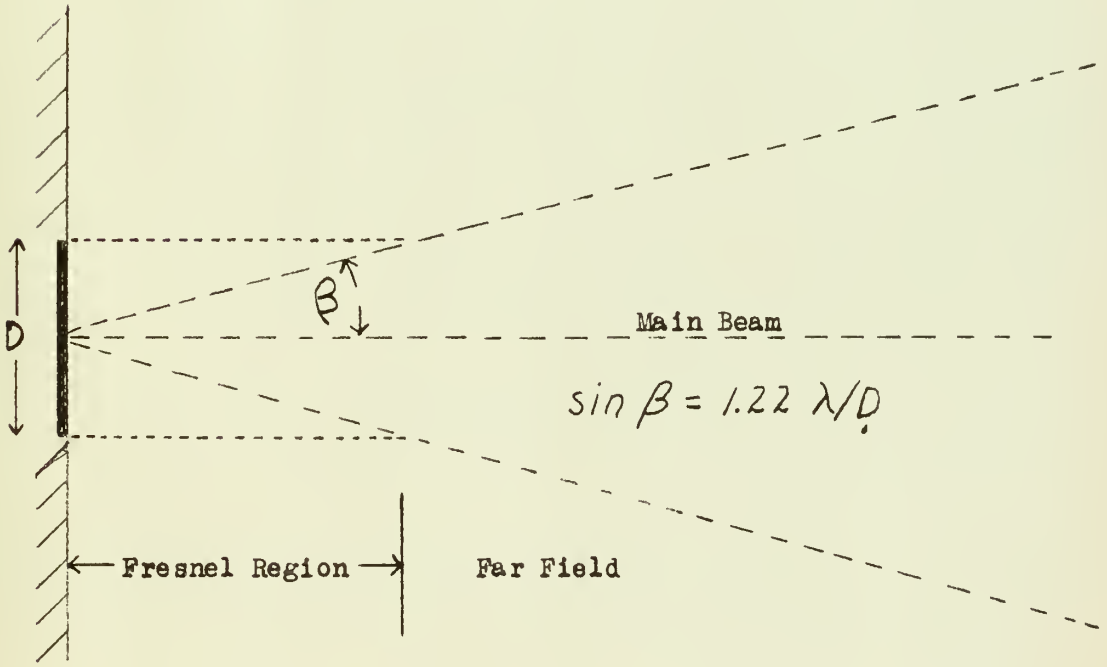

Figure 2. Fresnel region and far field for energy radiated from a plane transducer.

the acoustic velocity in the medium. A fundamental frequency of 5 megacycles requires a transducer of 0.55 millimeters thickness, assuming an acoustic velocity of 5.5×10^3 meters per second. The barium titanate ceramics are permanently polarized by slow cooling from slightly above the Curie temperature (120° C) to room temperature, while applying a direct current voltage of 6,000 volts per centimeter thickness across the ceramic.

When a sound wave is generated by a plane piston transducer a number of wave lengths across, there is a region, called the Fresnel region, for which the wave front is essentially plane as shown in Figure 2. For an infinite medium, the energy then spreads out at an angle β determined by the equation $\sin \beta = 1.22 \lambda/D$, and the pressure decreases proportional to the distance from the source. It is therefore necessary to limit sample length to the Fresnel region in order to eliminate the pressure losses due to divergence of the acoustic field beyond this region. The Fresnel region of a 9.3 megacycle sound wave generated in cyclohexane may be calculated from the measured velocity (1520 meters per second) and the transducer diameter (1.28 centimeters).

$$\lambda = c/f = \frac{1.52 \times 10^5 \text{ cm. sec.}^{-1}}{9.3 \times 10^6 \text{ sec.}^{-1}} = 0.016 \text{ cm.}$$

$$\sin \beta = 1.22 \left(\frac{.016}{1.28}\right) = 0.0153.$$

Using the small angle approximation, $\sin\beta = \tan\beta$.

Fresnel region length = Radius/$\tan\beta$ = 0.64/.0153 = 42 cm.

Calculations thus made of the plane wave region involved in the cyclohexane measurements show the minimum Fresnel region to be 32 centimeters which is

several times the length of the longest sample measured.

Seki, Granato and Truell (5) have recently shown that the diffraction attenuation of a piston source is of the order of magnitude of one decibel per a^2/λ , where a is the piston radius and λ is the acoustic wave length in the medium. The diffraction loss for a 9.3 megacycle sound wave in cyclohexane is: $\lambda/8.68\ a^2 = .016/8.68\ (.64)^2 = .0045\ cm^{-1}$. The contribution of the diffraction effects to the attenuation constant can therefore be calculated and the maximum value thus obtained for the cyclohexane measurements is found to be 0.006 per centimeter; a value quite insignificant when compared to the order of magnitude of the attenuation constant obtained.

The detail of the arrangement of barium titanate transducers utilized in this investigation is shown in Figure 3. The transducers are cemented with rubber cement to thin strips of sponge rubber which in turn are cemented to the parallel faces of the supporting bar. The sponge rubber serves the dual purpose of preventing back relections as well as being a cushion for the fragile ceramics. Two short pieces of a copper wave guide are silver soldered to brass collars machined to serve as a bearing surface to slide on the steel guide rods. This arrangement is quite versatile for mounting specimens in any position and also small enough to permit measurements to be made in a refrigerator as necessitated by the low melting point of cyclohexane (6.5° C). A narrow strip of the silvered surface is removed at the circumference of the rear face of the ceramics. This technique of extending the front surface around the edge permits electrical contact to be made by pressure contact using fine spring wire, and leaves the contact surface free from interfering electrical connections. A similar wire connection is made through the BNC connector to the rear face of the ceramic.

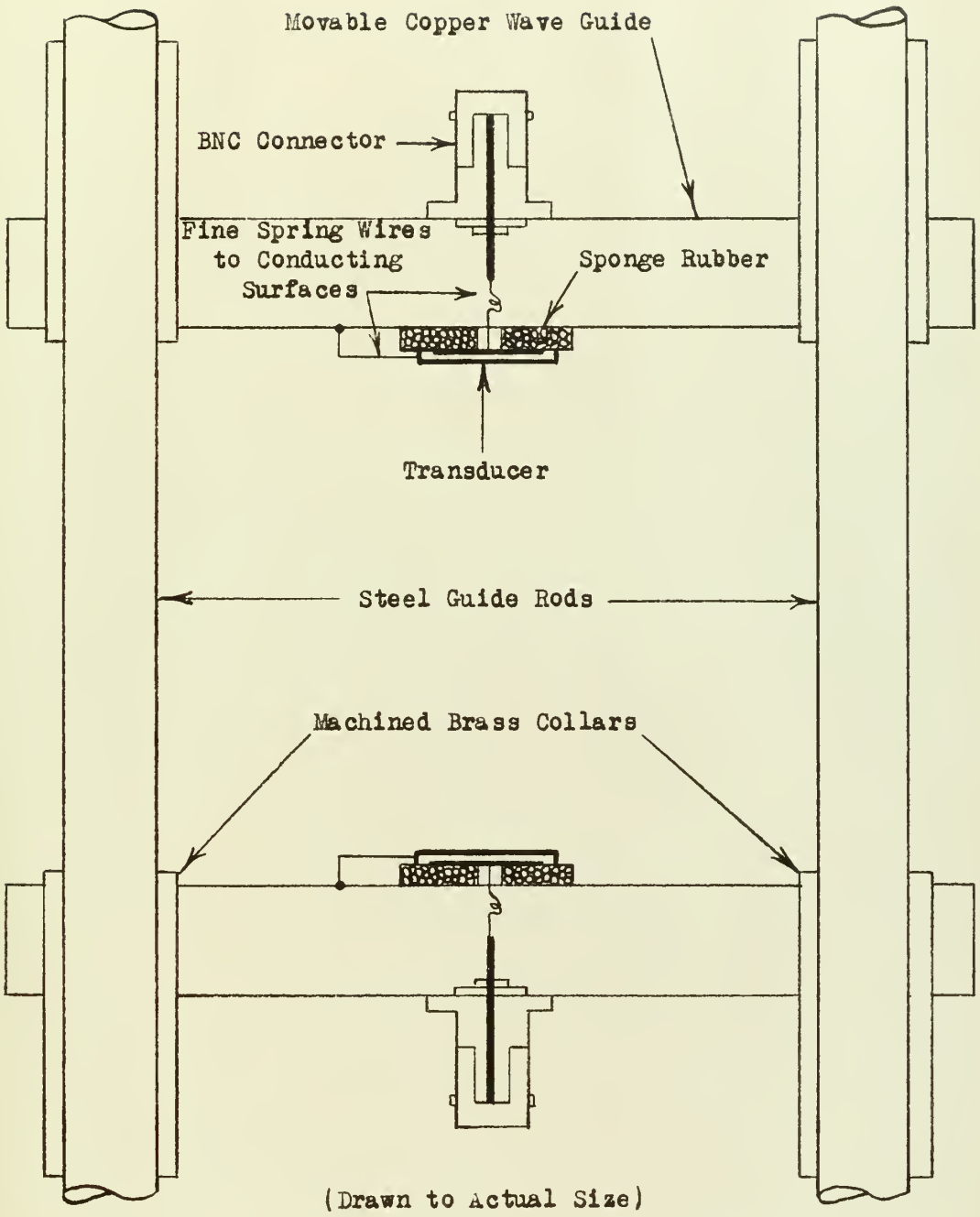

Figure 3. Arrangement of barium titanate transducers utilized in ultrasonic pulsing method.

The crystalline cyclohexane samples are grown on a cold finger which is immersed in a melt of liquid cyclohexane maintained at a temperature slightly above the melting point. A large reservoir of an ethylene glycol-water solution is utilized as a heat sink to remove the latent heat of fusion of the crystal growth process. A small centrifugal pump is used to circulate the cold reservoir solution through the cold finger. At the commencement of solid growth a small temperature differential is maintained and following the growth of a solid layer of cyclohexane on the cold finger, a greater temperature differential is required to continue the growth because of the low thermal conductivity of this material. The samples are removed from the cold finger, after suitable growth is obtained, and are surfaced by contact melting utilizing glass plates, prior to measurement of the ultrasonic attenuation. The crystalline cyclohexane is found to be very fragile and extreme care must be exercised to prevent cracking in a specimen in preparing it for making measurements.

3. Results.

A summary of the measurements obtained in lucite, polystyrene and cyclohexane is presented in Table I. The velocity of the acoustic wave

TABLE I. Ultrasonic measurements in solid media.

Material	Frequency in Megacycles per Second					
	2.3		3.85		9.3	
	α*	c**	α	c	α	c
Lucite	0.45	2100	0.79	2320	1.85	2440
Polystyrene	0.15	-	0.18	2320	0.60	2320
Cyclohexane	0.18	-	0.25	1520	0.45	1520

* Attenuation constant, nepers per centimeter
** Velocity, meters per second

was observed to increase with frequency in the case of lucite and appeared to remain constant in polystyrene and cyclohexane. The acoustic velocity in cyclohexane was observed to be 1520 meters per second while in lucite and polystyrene the velocity was approximately 2300 meters per second. The attenuation constant was observed to be of the same order of magnitude in both cyclohexane and polystyrene over the frequency range utilized and was considerably larger in lucite. The measurements for lucite and polystyrene were conducted at room temperature and the cyclohexane samples were measured at approximately 0° C. Figure 4 illustrates the photographic record of the measurements obtained utilizing a fundamental frequency of 3.85 megacycles in polystyrene and Figure 5 presents the same record for cyclohexane. Two different sample lengths were utilized for every attenuation measurement.

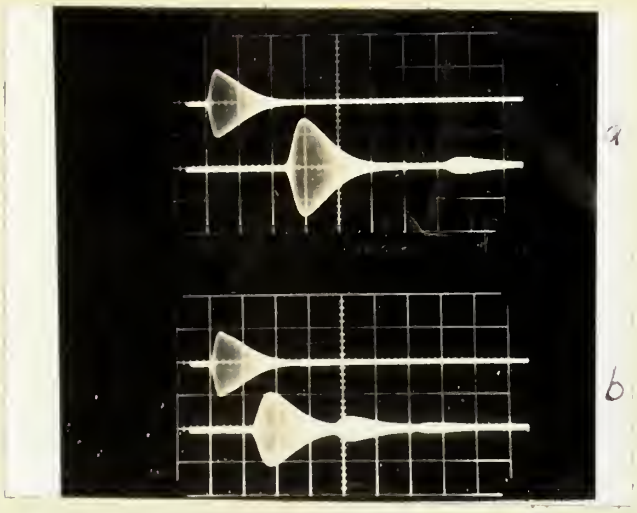

Figure 4. Absorption measurements in polystyrene at 3.85 megacycles, input pulse is shown in the upper trace. (a) Input pulse: 10 volts per scale division. Output pulse: 1 volt per scale division. Time: 10 microseconds per scale division. Sample length: 5.55 centimeters. (b) Input pulse: 10 volts per scale division. Output pulse: 2 volts per scale division. Time: 10 microseconds per scale division. Sample length: 2.90 centimeters.

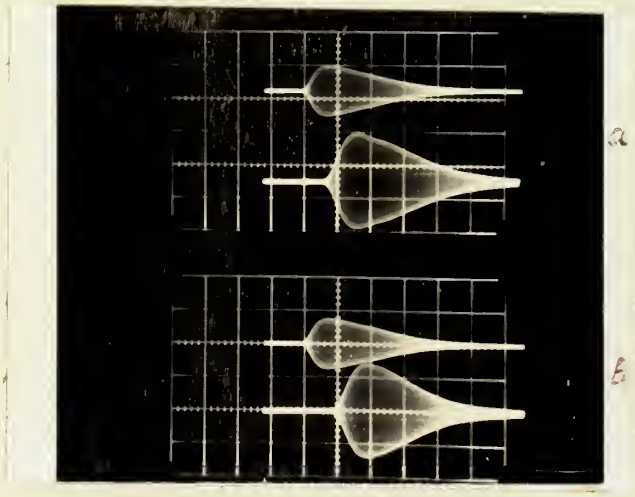

Figure 5. Abosrption measurements in cyclohexane at 3.85 megacycles, input pulse is shown in the upper trace. (a) Input pulse: 10 volts per scale division. Output pulse: 1 volt per scale division. Time: 5 microseconds per scale division. Sample length: 0.46 centimeters. (b) Same scale values as in (a). Sample length: 0.73 centimeters.

4. Discussion.

The measurements with lucite and polystyrene were primarily performed so as to enable comparison of the results with data previously published (1), and thus allow a check on the experimental procedure to be made. Good agreement was obtained for both attenuation and velocity determinations.

The attenuation constant for cyclohexane is found to vary as the two-thirds power of the applied frequency, as determined from the slope of the log-log plot of frequency versus attenuation constant shown in Figure 6. This result is believed to be an indication that cyclohexane does not exhibit the same molecular resonance absorption phenomenon that benzene does in the frequency range studied. The reliability of the measurements performed using cyclohexane is indeterminate because of the limited number of samples measured.

Liebermann (3) has shown that the attenuation constant for benzene varies as the square of the applied frequency in the 6.4 - 10 megacycle range. The fact that the attenuation constant of cyclohexane is not observed to vary as the square of the applied frequency is not considered sufficient evidence to eliminate possible resonance absorption in the molecular crystal. The order of magnitude of the measured absorption in cyclohexane is similar to that reported by Liebermann for benzene, which is orders of magnitude higher than has been observed in other crystalline substances. The cyclohexane samples used in this investigation are believed to be polycrystalline samples rather than a single crystal, a factor that could well account for the difference in the measurements between cyclohexane and benzene. Liebermann reported the use of a single crystal for the determinations made with benzene.

It would be of interest to extend the absorption measurements in cyclohexane over a greater frequency range as well as investigating a possible

change in absorption processes at lower temperatures. With the aid of better crystal growing techniques, similar measurements in a single crystal of cyclohexane would also be of interest.

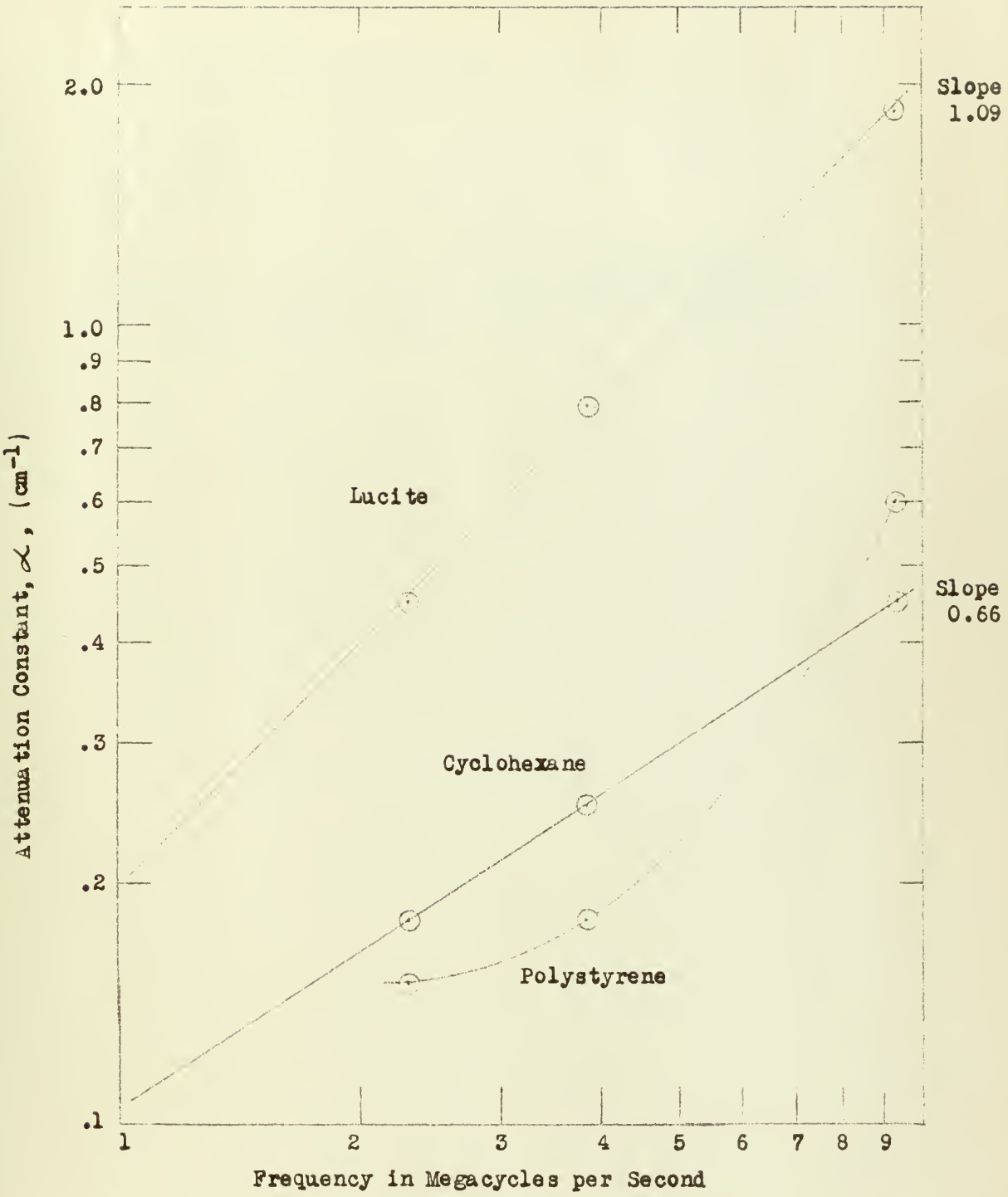

Figure 6. Attenuation constant versus frequency of ultrasonic waves in solid media.

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